

(12) UK Patent Application (19) GB (11) 2 285 634 (13) A

(43) Date of A Publication 19.07.1995

(21) Application No 9426370.4

(22) Date of Filing 22.12.1994

(30) Priority Data

(31) 05335123
05335868

(32) 28.12.1993
28.12.1993

(33) JP

(71) Applicant(s)

Nippon Sheet Glass Co., Ltd

(Incorporated in Japan)

5-11 Dosho-Machi 3-Chome, Chuo-Ku, Osaka-Shi,
Osaka-Fu, Japan

(72) Inventor(s)

Akira Fujisawa
Hodaka Norimatsu
Jun Yamaguchi
Kouichi Ataka

(51) INT CL⁶

C03C 17/25, C23C 18/12

(52) UK CL (Edition N)

C7F FHB FR908 FR914 F782
U1S S1403 S1714 S1855

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WPI Abstract Accession No. 82-91184E/43 & JP
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(58) Field of Search

UK CL (Edition N) C7F FHB FHD FHE
INT CL⁶ C03C 17/23 17/245 17/25, C23C 16/40 18/12
ONLINE: WPI, CLAIMS

(74) Agent and/or Address for Service

Marks & Clerk
Alpha Tower, Suffolk Street Queensway,
BIRMINGHAM, B1 1TT, United Kingdom

(54) Heat ray-reflecting glass with coating film of cobalt oxide and nickel oxide

(57) A heat ray-reflecting glass comprises a glass substrate having on the surface thereof a coating film comprising cobalt oxide and nickel oxide.

In a first aspect the coating film has a surface resistivity of not less than $10^4 \Omega/\text{square}$ and a thickness of not less than 10 nm, the content of cobalt in the coating film based on the total metal content per unit area is from 60 to 90% by weight, and the content of nickel in the coating film based on the total metal content per unit area is from 10 to 40% by weight.

In a second aspect the coating film further comprises a metal oxide containing at least one metal selected from titanium, vanadium, chromium, manganese, copper, and zirconium, and has a surface resistivity of not less than $10^4 \Omega/\text{square}$ and a thickness of not less than 10 nm, the content of cobalt in the coating film based on the total metal content per unit area is from 60 to 89% by weight, the content of nickel in the coating film based on the total metal content per unit area is from 10 to 39% by weight, and the content of at least one metal selected from titanium, vanadium, chromium, manganese, copper, and zirconium in the coating film based on the total metal content per unit area is from 1 to 30% by weight.

In a third aspect the coating film further comprises an iron oxide, and has a surface resistivity of not less than $10^4 \Omega/\text{square}$ and a thickness of not less than 10 nm, and the content of iron in the coating film based on the total metal content per unit area is from 1.0 to 4.5% by weight.

In a fourth aspect the coating film has a surface resistivity of not less than $10^4 \Omega/\text{square}$ and a thickness of from 10 to 70 nm, and consisting essentially of oxides having spinel structures comprising cobalt oxide and nickel oxide, and a reflecting color tone viewed from the side of said heat ray-reflecting glass opposite to said coating film being green series color.

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Fig. 1

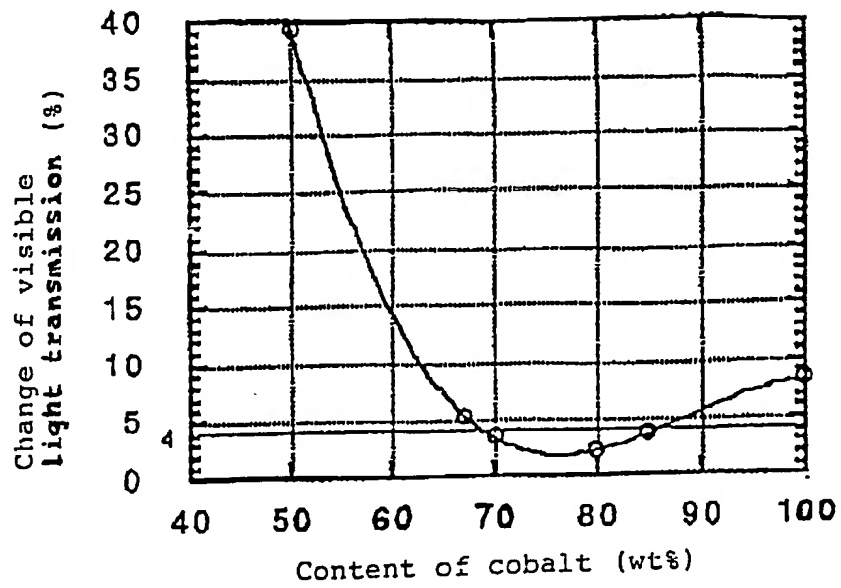
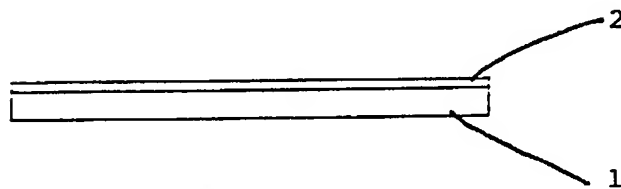


Fig. 2



HEAT RAY-REFLECTING GLASS

This invention relates to heat ray-reflecting glass for buildings, automobiles and other vehicles.

Heat ray-reflecting glass having low transmission of visible light and solar radiation has recently been extending its use as window panes for buildings and automobiles for the purpose of reducing the heat of direct sunlight, reducing the burden of air conditioners, protecting privacy, and improving appearance. Heat ray-reflecting glass is produced by forming on a glass substrate a metal film or a metal nitride film by a physical means, such as sputtering, or forming a metal oxide film by spraying a film-forming solution containing a metal compound onto the surface of the glass substrate heated above the thermal decomposition temperature of the metal compound. The latter method is superior to the former from the standpoint of production cost, durability of the coating film, and the like. However, the heat ray-reflecting glass obtained by this method hardly reduces a visible light transmission and a solar radiation transmission below a certain level depending on the composition of the coating film.

Under these circumstances, a coating film containing metal oxides of cobalt and nickel is known as a coating film capable of relatively reducing a visible light transmission,

etc. as described in JP-B-63-32736. (The term "JP-B" used herein means an examined Japanese patent publication.)

However, the coating film used in electrically conductive articles disclosed in JP-B-63-32736 has a small surface resistivity and therefore high electromagnetic wave reflectivity and, when used as a heat ray-reflecting pane in buildings, causes a ghost on a TV image in neighboring houses, which is a disadvantage in practical use particularly in towns and cities.

In the light of these circumstances, an object of the present invention is to provide heat ray-reflecting glass the coating film of which has electromagnetic wave reflectivity reduced to a level causing no problem in use, while retaining a certain range of optical characteristics possessed by a coating film containing cobalt oxide and nickel oxide, and also exhibits excellent durability.

The present invention relates to heat ray-reflecting glass comprising a glass substrate having on the surface thereof a coating film comprising cobalt oxide and nickel oxide.

The coating film has the following characteristics:

(1) In a first aspect of the present invention, the coating film has a surface resistivity of not less than $10^4 \Omega/\text{square}$ and a thickness of not less than 10 nm,

the content of cobalt in the coating film based on the total metal content per unit area is from 60 to 90% by weight, and

the content of nickel in the coating film based on the total metal content per unit area is from 10 to 40% by weight.

(2) In a second aspect of the present invention, the coating film further comprises a metal oxide containing at least one metal selected from titanium, vanadium, chromium, manganese, copper, and zirconium, and has a surface resistivity of not less than $10^4 \Omega/\text{square}$ and a thickness of not less than 10 nm,

the content of cobalt in the coating film based on the total metal content per unit area is from 60 to 89% by weight,

the content of nickel in the coating film based on the total metal content per unit area is from 10 to 39% by weight, and

the content of at least one metal selected from titanium, vanadium, chromium, manganese, copper, and zirconium in the coating film based on the total metal content per unit area is from 1 to 30% by weight.

(3) In a third aspect of the present invention,

the coating film further comprises an iron oxide, and has a surface resistivity of not less than $10^4 \Omega/\text{square}$ and a thickness of not less than 10 nm, and

the content of iron in the coating film based on the total metal content per unit area is from from 1.0 to 4.5% by weight.

(4) In a fourth aspect of the present invention, the coating film has a surface resistivity of not less than $10^6 \Omega/\text{square}$ and a thickness of from 10 to 70 nm, and consisting essentially of oxides having spinel structures comprising cobalt oxide and nickel oxide, and

a reflecting color tone viewed from the side of said heat ray-reflecting glass opposite to said coating film being green series color.

Fig. 1 shows the relationship between the content of cobalt to the total metal content per unit area of a coating film and change of visible light transmission before and after an acid resistance test.

Fig. 2 shows a schematic cross section of the heat ray-reflecting glass according to the present invention, in which the numeral 1 denotes a glass substrate, and 2 denotes the coating film.

The heat ray-reflecting glass according to the present invention can be produced by a method comprising applying a film-forming solution containing a cobalt compound, a nickel compound, and other compounds for constituting the components of the coating film to a glass substrate kept at a temperature not lower than the thermal decomposition temperature of these metallic compounds to form

a metal oxide film. More specifically, the method can be effected by spraying the film-forming solution onto glass maintained at a high temperature after melt forming on the glass manufacturing line by the float method.

The temperature of the glass substrate at which a film-forming solution is applied is preferably from 350 to 800°C.

Examples of the cobalt compounds include cobalt (II) or (III) acetylacetonate, cobalt acetate, cobalt chloride, cobalt borate, cobalt sulfate, cobalt benzoate, cobalt bromide, cobalt nitrate, cobalt fluoride, cobalt iodide, cobalt oxalate, cobalt phosphate, cobalt phosphite, and cobalt stearate.

Examples of the nickel compounds include dipropionylmethanenickel, dipropionylacetonenickel, nickel acetylacetonate, nickel acetate, nickel bromide, nickel chloride, nickel fluoride, nickel fluorosilicate, nickel nitrate, nickel formate, nickel hydroxide, nickel iodide, nickel stearate, nickel sulfamate, and nickel sulfate.

Among these nickel compounds preferred are dipropionylmethanenickel and/or dipropionylacetonenickel which can provide a coating film with a satisfactory appearance and have satisfactory solubility in organic solvents, such as alcohols, toluene, and xylene.

Nickel acetylacetonate forms a coating film having further improved appearance and can also preferably be used in

the present invention. Since nickel acetylacetonate has low solubility in organic solvents, such as alcohols, toluene, and xylene, it is preferably used in the form of a suspension in an organic solvent.

Examples of the titanium compounds include titanium tetrachloride, titanium tetraethoxide, titanyl acetylacetonate, titanium (III) sulfate, titanium (IV) sulfate, titanium tetrabutoxide, titanium isopropoxide, titanium methoxide, titanium diisopropoxybisoctyleneglycoxide, titanium di-n-propoxybisoctyleneglycoxide, diisopropoxymonooctyleneglycoxyacetylacetonatotitanium, di-n-butoxymonooctyleneglycoxyacetylacetonatotitanium, titanium tetraoctyleneglycoxide, and di-n-propoxybisacetylacetonatotitanium.

Examples of the vanadium compounds include vanadium acetylacetonate, vanadyl acetylacetonate, vanadium trichloride, vanadyl dichloride, vanadyl trichloride, vanadyl nitrate, vanadyl oxalate, and vanadyl sulfate.

Examples of the chromium compounds include chromium acetylacetonate, chromium (III) acetate, chromium (II) chloride, chromium (III) chloride, chromium (III) formate, chromium (III) fluoride, ammonium chromium sulfate, chromium (III) hydroxide, chromium (III) nitrate, chromium (III) phosphate, potassium chromium sulfate, and chromium (III) sulfate.

Examples of the manganese compounds include manganese (I) acetylacetonate, manganese (II) acetylacetonate, manganese acetate, ammonium manganese sulfate, manganese borate, manganese bromide, manganese carbonate, manganese chloride, manganese fluoride, manganese fluorosilicate, manganese formate, manganese iodide, manganese lactate, manganese nitrate, manganese oxalate, manganese dihydrogenphosphate, manganese hydrogenphosphate, manganese sulfate, and manganese tartrate.

Examples of the copper compounds include copper acetylacetonate, cuprous bromide, cupric bromide, cuprous chloride, cupric chloride, ammonium cupric chloride, cupric citrate, cuprous cyanide, copper fluoroborate, cupric fluoride, copper fluorosilicate, cupric formate, cupric hydroxide, cuprous iodide, copper nitrate, copper oleate, cupric oxalate, cupric phosphate, and copper sulfate.

Examples of the zirconium compounds include zirconium acetylacetonate, zirconium hydroxide, zirconium nitrate, zirconium nitrite, zirconium oxychloride, zirconium oxyphosphate, zirconium sulfate, zirconium tetrachloride, and zirconium acetate.

Examples of the iron compounds include iron acetylacetonate, ferrous chloride, ferric chloride, ferric citrate, ammonium ferric oxalate, ammonium ferric sulfate, iron fluoroborate, ferric fluoride, iron fluorosilicate, ferrous lactate, ferric nitrate, ferrous oxalate, ferrous

phosphate, ferric phosphate, ferrous sulfate, ferric sulfate, and ferrous tartrate.

As a solvent for dissolving or dispersing the above-mentioned metallic compounds, organic solvents such as aromatic solvents, ester solvents, ketone solvents, alcohol solvents, ether solvents can generally be used.

Examples of the glass substrate generally includes a colorless transparent soda-lime glass substrate but is not limited thereto. For adjusting a visible light transmission or a color tone of transmitted light, colored soda-lime glass containing a slight amount of coloring agents may also be used.

In order to reduce the reflectance, the coating film may further contain silicon or aluminum. In order to adjust the color tone, the coating film may further contain zinc, tin, antimony, indium, etc. The content of these metals for reducing the reflectance or adjusting the color tone is preferably 3% by weight or less based on the total metal content per unit area.

In the coating film according to the first aspect of the present invention, the content of cobalt in the coating film based on the total metal content per unit area is preferably from 68 to 87% by weight, and the content of nickel in the coating film based on the total metal content per unit area is preferably from 13 to 32% by weight, from the viewpoint of the durability of the coating film.

The coating film according to the first and second aspects of the present invention preferably has a thickness of not more than 130 nm, because if the thickness is too large, the surface resistivity may be less than $10^4 \Omega/\text{square}$ depending on its composition. The thickness is more preferably not more than 100 nm from the viewpoint of the productivity of the heat ray-reflecting glass, and is further preferably not more than 45 nm from the viewpoint of the transmittance of visible lights.

The thickness of the coating film according to all the aspects of the present invention is still preferably from 20 to 45 nm, because the coating film having the thickness of this range provides excellent appearance. The thickness is still further preferably from 20 to 40 nm. By using heat ray-reflecting glass having the coating film having such a thickness for windows of buildings, discomfort due to reflection of room illuminants at night can be suppressed because the reflecting color tone on the side of the coating film becomes monotone; and pollution due to reflected lights at outer walls of buildings can also be suppressed because the reflectance of the heat ray-reflecting glass at both the side of the coating film and the side opposite to the coating film can be reduced.

In the coating film according to the third aspect of the present invention, the content of nickel in the coating film based on the total metal content per unit area is

preferably from 5 to 40% by weight from the viewpoint of adjustment of visible light transmittance and improvement in durability of the coating film.

The heat ray-reflecting glass according to the present invention preferably exhibits a transmitted color tone as specified according to JIS Z8722-1982 falling within the following ranges:

$$-4.5 \leq a^* \leq 4.5$$

$$3.0 \leq b^* \leq 12.5$$

The above-specified transmitted color still preferably falls within the following ranges in view of the product value of the appearance of the heat ray-reflecting glass:

$$-0.5 \leq a^* \leq 0.5$$

$$5.0 \leq b^* \leq 8.5$$

The reflected visible light viewed from the side of the heat ray-reflecting glass opposite to the coating film preferably exhibits a reflected color tone as specified according to JIS Z8722-1982 falling within the following ranges:

$$-7.0 \leq a^* \leq -3.0$$

$$-5.0 \leq b^* \leq 4.0$$

a^* and b^* used herein are chromaticness indexes according to the $L^*a^*b^*$ colorimetric system specified in JIS Z8729-1980.

The heat ray-reflecting glass according to the first aspect of the present invention has a surface resistivity of $10^4 \Omega/\text{square}$ or higher so that the electromagnetic wave reflection is inhibited to such an extent that gives rise to substantially no problem in practical use. While the surface resistivity increases according as the film thickness is decreased, with the composition of the film being equal, the lower limit of the coating film of the first aspect of the present invention is set at 10 nm so as to retain the optical performance properties essential to heat ray-reflecting glass. Further, the visible light transmission and solar radiation transmission of the heat ray-reflecting glass of the first aspect of the present invention are controlled within practically favorable ranges by limiting the contents of cobalt oxide and nickel oxide. That is, in a coating film containing cobalt oxide and nickel oxide, nickel cobaltite having a spinel structure decreases the surface resistivity. Therefore, while the resistivity of a coating film may be increased by making the ratio of nickel to cobalt largely different from the stoichiometric ratio of nickel cobaltite ($\text{Ni/Co} = 1/2$), if this means for increasing resistivity is applied to the case in which the proportion of cobalt oxide is less than 60%, there is a possibility that a visible light transmission may exceed 50%. On the other hand, when the means is applied to the case in which the proportion of nickel oxide is less than 10%, the solar radiation

transmission of the glass could not be so reduced as the visible light transmission. In both cases, the features of the coating film are not manifested. In the first aspect of the present invention, therefore, such a problem is avoided by specifying the weight percentages of cobalt and nickel to the total metal content per unit area of the coating film so as to fall within the range of from 60 to 90% and the range of from 10 to 40%, respectively.

The heat ray-reflecting glass according to the second aspect of the present invention exhibits the above-mentioned characteristic features of the first aspect of the present invention, and further the durability is improved since the coating film of the second aspect of the present invention contains at least one metal selected from titanium, vanadium, chromium, manganese, copper, and zirconium.

The heat ray-reflecting glass according to the third aspect of the present invention also has a surface resistivity of $10^4 \Omega/\text{square}$ or higher so that the electromagnetic wave reflection is inhibited to such an extent that gives rise to substantially no problem in practical use. In the coating film of the third aspect of the present invention, the lower limit of the thickness is set at 10 nm so as to retain the optical performance properties essential to heat ray-reflecting glass, and the upper limit of the thickness is set at 70 nm so as to attain the surface resistivity of $10^4 \Omega/\text{square}$ or higher without

using a relatively large amount of iron. Accordingly, the content of iron in the coating film according to the third aspect of the present invention can be reduced to 4.5% by weight or lower so as to improve the durability, particularly acid resistance, of the coating film.

The heat ray-reflecting glass according to the fourth aspect of the present invention also has a surface resistivity of $10^4 \Omega/\text{square}$ or higher so that the electromagnetic wave reflection is inhibited to such an extent that gives rise to substantially no problem in practical use. In the heat ray-reflecting glass of the fourth aspect of the present invention, the reflected color tone viewed from the side opposite to the coating film is green series color. Therefore, it can be utilized as the heat ray-reflecting glass having green reflected color tone, which has been demanded as those for windows of buildings from the viewpoint of accordance in color tone of buildings and surrounding scene. Conventional heat ray-reflecting glass having green reflected color tone includes glass having three-layered film composed of titanium oxide and titanium nitride, as described in JP-A-63-190742. (The term "JP-A" used herein means an unexamined Japanese patent application.) Since this conventional heat ray-reflecting glass is produced by forming the coating film by physical vapor deposition, it is inferior in productivity to the heat ray-reflecting glass of the fourth aspect of the present invention in which a

coating film of high durability can be produced in a low cost. An oxide film having the same spinel structures as in the fourth aspect of the present invention but composed of cobalt, chromium and iron can be produced by thermal decomposition of a film forming solution. However, the coating film having such a composition cannot exhibit green reflected color tone even if its thickness is adjusted. In this case, even though color tone near the green region can be obtained, it is difficult to obtain uniform color tone by forming a uniform coating film on a wide area.

The heat ray-reflecting glass according to the first, second and third aspects of the present invention can exhibit green reflected color tone as similar to the fourth aspect of the present invention by adjusting the coating film, specifically by making the thickness of the coating film to 70 nm or lower.

The present invention will be described in more detail by reference to the following examples and comparative examples, but the present invention is not construed as being limited to the examples.

Example 1

A 150 mm long, 150 mm wide, and 4 mm thick soda-lime silica glass plate was washed and dried to prepare a substrate. The substrate was fixed with a hanger in an electric oven set at 650°C and maintained for 5 minutes. A coating solution composed of 5.13 g of cobalt (III)

acetylacetonate and 1.18 g of dipropionylmethanenickel (II) dissolved in 100 cc of toluene was sprayed onto the substrate taken out of the electric oven by using a commercially available spraygun at an air pressure of 3.0 kg/cm², an air flow of 90 l/min, and at a rate of spray coating of 20 ml/min for about 10 seconds.

The visible light transmission, visible light reflectance, solar radiation transmission, and solar radiation reflectance of the resulting heat ray-reflecting glass was measured in accordance with JIS R 3106-1985. The cobalt content based on the total metal content in the coating film was measured by radiofrequency plasma emission spectroscopy. The surface resistivity and thickness of the coating film were measured. The results obtained are shown in Table 1 below.

Example 2

Heat ray-reflecting glass was prepared in the same manner as in Example 1, except that the amount of cobalt (III) acetylacetonate was changed to 4.27 g, the amount of dipropionylmethanenickel (II) was changed to 1.96 g, the time for spraying was changed to about 15 seconds, and the rate of spray coating was changed to 24 ml/min. The resulting heat ray-reflecting glass was examined in the same manner as in Example 1. The results obtained are shown in Table 1.

Example 3

Heat ray-reflecting glass was prepared in the same manner as in Example 1, except that the amount of cobalt (III) acetylacetonate was changed to 3.21 g, the amount of dipropionylmethanenickel (II) was changed to 2.94 g, the time for spraying was changed to about 20 seconds, and the rate of spray coating was changed to 28 ml/min. The resulting heat ray-reflecting glass was examined in the same manner as in Example 1. The results obtained are shown in Table 1.

Comparative Example 1

For comparison, a coating film composed of metallic oxides of chromium, iron and cobalt was formed to produce heat ray-reflecting glass. Heat ray-reflecting glass was prepared in the same manner as in Example 1, except that the amount of cobalt (III) acetylacetonate was changed to 6.55 g, 1.90 g of iron (III) acetylacetonate and 5.00 g of chromium (III) acetylacetonate were used instead of dipropionylmethanenickel (II), the time for spraying was changed to about 30 seconds, and the rate of spray coating was changed to 35 ml/min. The resulting heat ray-reflecting glass was examined in the same manner as in Example 1. The results obtained are shown in Table 1.

TABLE 1

	Thickness of coating film (nm)	Cobalt content (wt%)	Visible light transmission (%)	Visible light reflectance (%)	Solar radiation transmission (%)	Solar radiation reflectance (%)	Surface resistivity (k Ω /square)
Example 1	26	87	41.1	23.7	43.6	20.3	51
Example 2	23	78	44.0	22.0	45.1	19.0	29
Example 3	18	62	50.0	22.3	51.2	18.5	170
Comparative Example 1	88	63	32.3	32.6	37.2	35.0	-

It is understood from the results of Table 1 that heat ray-reflecting glass of Examples 1 to 3 has a surface resistivity of 10^4 Ω /square or more and a visible light transmission of 50% or less, and the solar radiation transmission does not exceed the value 2.5% higher than the visible light transmission. In the heat ray-reflecting glass of Comparative Example 1, the visible light transmission is suppressed to 50% or less, but the solar radiation transmission is almost 5% higher than the visible light transmission. Accordingly, the heat ray-reflecting glass of Examples 1 to 3 are excellent in solar radiation shielding performance in comparison to that of Comparative Example 1.

The chromaticness index a^* and b^* of the transmitted light of the heat ray-reflecting glass obtained in Examples 2 and 3 and Comparative Example 1 were measured. The results are shown in Table 2 below.

TABLE 2

	<u>a^*</u>	<u>b^*</u>
Example 2	0.28	8.29
Example 3	-0.13	8.41
Comparative Example 1	-0.72	13.80

Examples 4 to 8 and Comparative Example 2 and 3

Heat ray-reflecting glass was prepared in the same manner as in Example 1 except that the composition of the coating solution was changed. The visible light transmission, visible light reflectance, solar radiation transmission, and solar radiation reflectance of the resulting heat ray-reflecting glass was measured in accordance with JIS R 3106-1985. Further, the chemical resistance was examined in accordance with JIS R 3221-1990, provided that the time for immersing the glass in chemical was 3 days.

The results obtained are shown in Table 3 and Fig. 1.

TABLE 3

	Thickness of coating film (nm)	Cobalt content (wt%)	Visible light transmission (%)	Solar radiation transmission (%)	Surface resistivity (k Ω /square)	Durability*	
						Acid (%)	Base (%)
Example 4	30	80	41.1	43.6	51	2.3	0.0
Example 5	30	70	42.0	43.5	48	3.6	0.0
Example 6	25	85	44.5	47.2	70	3.9	0.0
Example 7	25	67	44.0	45.1	29	5.4	0.0
Example 8	25	80	43.8	46.2	63	3.4	0.0
Comparative Example 2	25	50	50.3	51.2	170	39.4	0.0
Comparative Example 3	30	100	42.5	47.3	250	8.3	0.0

Note: * Durability: change in transmission before and after immersion in chemicals

It is understood from Fig. 1 that the acid resistance of the coating film is particularly excellent in the region in that the cobalt content is from 68 to 87% by weight.

It is understood from the results in Table 3 that the metallic oxide coating film having a cobalt content of 50% by weight has a visible light transmission of more than 50%, but the metallic oxide coating film having a cobalt content of 100% by weight has a solar radiation transmission of about 5% higher than the visible light transmission, thus failing to attain a sufficient transmission energy controlling performance.

In all Examples 1 to 8, coating films having uniform appearance were obtained.

While in Examples 1 to 8, colorless transparent soda-lime glass was used as the glass substrate, the visible light transmission, the solar radiation transmission, the transparent color tone of the resulting heat ray-reflecting glass can be properly adjusted by using colored soda-lime glass as the substrate.

Comparative Example 4

Heat ray-reflecting glass was prepared in the same manner as in Example 1, except that the amount of cobalt (III) acetylacetonate was changed to 7.12 g, the amount of dipropionylmethanenickel (II) was changed to 3.13 g, the amount of toluene was changed to 200 cc, the time for spraying was changed to about 50 seconds, and the rate of

spray coating was changed to 100 ml/min. The resulting heat ray-reflecting glass had a coating film having a thickness of 150 nm, and the visible light transmission was 8.5%, but the surface resistivity was 1,100 Ω /square.

Example 9

A 150 mm long, 150 mm wide, and 4 mm thick soda-lime silica glass plate was washed and dried to prepare a substrate. The substrate was fixed with a hanger in an electric oven set at 650°C and maintained for 5 minutes. A coating solution composed of 5.13 g of cobalt (III) acetylacetonate, 1.18 g of dipropionylmethanenickel (II), and 0.65 g of vanadium acetylacetonate dissolved in 100 cc of toluene was sprayed onto the substrate taken out of the electric oven by using a commercially available spraygun at an air pressure of 3.0 kg/cm², an air flow of 90 l/min, and at a rate of spray coating of 20 ml/min for about 20 seconds.

The visible light transmission of the resulting heat ray-reflecting glass was measured in accordance with JIS R 3106-1985. The cobalt content based on the total metal content in the coating film was measured by radiofrequency plasma emission spectroscopy. The surface resistivity and thickness of the coating film were measured. The results obtained are shown in Table 4 below.

Example 10

Heat ray-reflecting glass was prepared in the same manner as in Example 9, except that 0.66 g of chromium

acetylacetonate was used instead of vanadium acetylacetonate, and examined in the same manner as in Example 9. The results obtained are shown in Table 4.

Example 11

Heat ray-reflecting glass was prepared in the same manner as in Example 9, except that 0.66 g of manganese acetylacetonate was used instead of vanadium acetylacetonate, and examined in the same manner as in Example 9. The results obtained are shown in Table 4.

Example 12

Heat ray-reflecting glass was prepared in the same manner as in Example 9, except that 0.66 g of copper acetylacetonate was used instead of vanadium acetylacetonate, and examined in the same manner as in Example 9. The results obtained are shown in Table 4.

Example 13

Heat ray-reflecting glass was prepared in the same manner as in Example 9, except that 0.66 g of zirconium acetylacetonate was used instead of vanadium acetylacetonate, and examined in the same manner as in Example 9. The results obtained are shown in Table 4.

Comparative Example 5

Heat ray-reflecting glass was prepared in the same manner as in Example 9, except that zirconium acetylacetonate was not used, and examined in the same manner as in Example 9. The results obtained are shown in Table 4.

TABLE 4

	<u>Added element</u>	<u>Thickness of coating film (nm)</u>	<u>Visible light transmission (%)</u>	<u>Cobalt content (%)</u>	<u>Surface resistivity (kΩ/square)</u>
Example 9	vanadium	35	40.8	85	2,350
Example 10	chromium	29	44.5	82	216
Example 11	manganese	36	40.6	83	1,420
Example 12	copper	37	37.0	89	30
Example 13	zirconium	22	49.8	86	790
Comparative Example 5	-	26	41.1	87	51

It is understood from the results shown in Table 4 that the heat ray-reflecting glass of Examples 9 to 13 has a surface resistivity of 10^4 k Ω /square or more and a visible light transmission of 50% or lower, and when a metallic oxide of vanadium, chromium, manganese, or zirconium is added to the coating film, the surface resistivity greatly increases.

Example 14

Cobalt (II) acetylacetonate, nickel (II) acetylacetonate, and titanium acetylacetonate were mixed in a molar ratio of 78.4/19.6/2, and 15 g of the resulting mixture was added to 100 cc of toluene containing polyethylene glycol and polydimethylsiloxane as dispersants. The mixture was stirred for 10 seconds by using a paint shaker (produced by Eishin Co.) to obtain a coating solution.

A 300 mm long, 300 mm wide, and 4 mm thick soda-lime glass plate was washed and dried to prepare a substrate. The substrate was fixed with a hanger in an electric oven set at 650°C and maintained for 5 minutes. 15 g of the above coating solution was sprayed onto the substrate taken out of the electric oven by using a commercially available spraygun at an air pressure of 4 kg/cm², an air flow of 140 l/min, to form a metallic oxide coating film having a thickness of 50 nm.

The visible light transmission and solar radiation transmission of the resulting heat ray-reflecting glass was measured in accordance with JIS R 3106-1985. The surface

resistivity of the coating film was measured. The results obtained are shown in Table 5 below.

Examples 15 to 19

Heat ray-reflecting glass was obtained in the same manner as in Example 14 except that titanium acetylacetonate was replaced by the same amount of vanadium acetylacetonate, chromium acetylacetonate, manganese acetylacetonate, copper acetylacetonate, or zirconium acetylacetonate. The resulting heat ray-reflecting glass was examined in the same manner as in Example 14. The results obtained are shown in Table 5.

Comparative Example 6

Heat ray-reflecting glass was obtained in the same manner as in Example 14 except that titanium acetylacetonate was not used. The resulting heat ray-reflecting glass was examined in the same manner as in Example 14. The results obtained are shown in Table 5.

TABLE 5

	Added element	Visible light transmission (%)	Solar radiation transmission (%)	Surface resistivity (k Ω /square)	Acid resistance*		Alkali resistance*	
					2 days	3 days	2 days	3 days
Example 14	titanium	31.4	35.1	15.0	A	B	A	A
Example 15	vanadium	29.1	32.7	30.8	A	A	A	A
Example 16	chromium	31.0	35.0	12.0	A	A	A	A
Example 17	manganese	29.2	32.9	11.3	A	A	A	A
Example 18	copper	30.7	33.7	11.4	A	A	A	A
Example 19	zirconium	31.2	35.3	13.5	A	A	A	A
Comparative Example 6	-	30.1	33.2	10.9	B	C	A	A

Note: * A: no change; B: discoloration; C: peeling

It is understood from the results shown in Table 5 that the acid resistance of the heat ray-reflecting glass having a coating film of oxides of cobalt and nickel can be improved by adding a metallic oxide of titanium, vanadium, chromium, manganese, copper, or zirconium to the coating film. The effect of improving the acid resistance is considerable in cases of vanadium, chromium, manganese, copper, or zirconium. It is further understood from the comparison between Examples 15 to 19 added with an oxide of titanium, etc. and Comparative Example 6 using no additional metallic oxide that the heat ray-reflecting glass of Examples 15 to 19 is improved in the durability of the coating film, particularly the acid resistance, with maintaining the visible light transmission and the solar radiation transmission within the certain ranges.

In all Examples 9 to 19, coating films having uniform appearance were obtained.

While in Examples 9 to 19, colorless transparent soda-lime glass was used as the glass substrate, the visible light transmission, the solar radiation transmission, the transparent color tone of the resulting heat ray-reflecting glass can be properly adjusted by using colored soda-lime glass as the substrate.

Example 20

A 150 mm long, 150 mm wide, and 6 mm thick soda-lime silica glass plate was washed and dried to prepare a

substrate. The substrate was fixed with a hanger in an electric oven set at 650°C and maintained for 5 minutes. A coating solution composed of 5.3 g of cobalt (III) acetylacetonate, 1.2 g of dipropionylmethanenickel (II), and 0.3 g of iron (III) acetylacetonate dissolved in 200 cc of toluene was sprayed onto the substrate taken out of the electric oven by using a commercially available spraygun at an air pressure of 1.5 kg/cm², an air flow of 50 l/min, and at a rate of spray coating of 100 ml/min for about 5 seconds.

The visible light transmission of the resulting heat ray-reflecting glass was measured in accordance with JIS R 3106-1985. The iron content and the nickel content based on the total metal content in the coating film was measured by radiofrequency plasma emission spectroscopy. The crystalline structure of the coating film was determined by X-ray diffraction spectroscopy. The surface resistivity of the coating film was measured by such a manner that the heat ray-reflecting glass was cut into 5x4 cm, silver paste was applied on the longer edge of 5 cm to a width of 0.5 cm to form an electrode, and the resistivity was measured with a digital multimeter. The wear resistance was measured by such a manner that a Taber truck wheel was rotated for 200 revolutions according to JIS R 3221-1990, and the difference in the haze values before and after the treatment was measured. The chemical resistance was measured by such a manner that the heat ray-reflecting glass was immersed in a

1 N sulfuric acid or a 1 N aqueous solution of sodium hydroxide at 40°C for 24 hours, and the deterioration of the coating film was evaluated to grade A, in which substantially no deterioration was observed, and grade B, in which obvious deterioration was observed. The results obtained are shown in Table 6 below.

Example 21

Heat ray-reflecting glass was prepared in the same manner as in Example 20, except that the thickness of the soda-lime silica glass as the substrate was changed to 12 mm. The resulting heat ray-reflecting glass was examined in the same manner as in Example 20. The results obtained are shown in Table 6.

Example 22

Heat ray-reflecting glass was prepared in the same manner as in Example 20, except that the amount cobalt (III) acetylacetonate was changed to 8.2 g, the amount of dipropionylmethanenickel (II) was changed to 1.2 g, and the amount of iron (III) acetylacetonate was changed to 0.4 g. The resulting heat ray-reflecting glass was examined in the same manner as in Example 20. The results obtained are shown in Table 6.

Example 23

Heat ray-reflecting glass was prepared in the same manner as in Example 20, except that the amount cobalt (III) acetylacetonate was changed to 4.5 g, the amount of

dipropionylmethanenickel (II) was changed to 1.2 g, and the amount of iron (III) acetylacetonate was changed to 0.3 g. The resulting heat ray-reflecting glass was examined in the same manner as in Example 20. The results obtained are shown in Table 6.

Comparative Example 7

Heat ray-reflecting glass was prepared in the same manner as in Example 20, except that the amount cobalt (III) acetylacetonate was changed to 5.3 g, the amount of dipropionylmethanenickel (II) was changed to 1.2 g, and the amount of iron (III) acetylacetonate was changed to 0.7 g. The resulting heat ray-reflecting glass was examined in the same manner as in Example 20. The results obtained are shown in Table 6.

Comparative Example 8

Heat ray-reflecting glass was prepared in the same manner as in Example 20, except that the amount cobalt (III) acetylacetonate was changed to 5.3 g, the amount of dipropionylmethanenickel (II) was changed to 1.2 g, the amount of iron (III) acetylacetonate was changed to 0.7 g, and the time for spraying was changed to twice that in Example 20. The resulting heat ray-reflecting glass was examined in the same manner as in Example 20. The results obtained are shown in Table 6.

Comparative Example 9

Heat ray-reflecting glass was prepared in the same manner as in Example 20, except that the amount cobalt (III) acetylacetonate was changed to 3.3 g, the amount of dipropionylmethanenickel (II) was changed to 2.9 g, and the amount of iron (III) acetylacetonate was changed to 0.1 g. The resulting heat ray-reflecting glass was examined in the same manner as in Example 20. The results obtained are shown in Table 6.

TABLE 6

	Thickness of coating film (nm)	Crystalline structure	Visible light transmission (%)	Surface resistivity (k Ω /square)	Iron content (%)	Nickel content (%)	Wear resistance (%)	Chemical resistance Acid Alkali
Example 20	25	spinel	35.7	1.4	4.2	21.7	0.8	A A
Example 21	30	spinel	33.6	2.6	1.9	20.7	0.9	A A
Example 22	22	spinel	32.1	3.2	3.8	8.3	0.7	A A
Example 23	33	spinel	45.8	10.8	1.2	36.8	1.1	A A
Comparative Example 7	27	spinel	34.9	3.5	6.7	21.4	0.8	B A
Comparative Example 8	75	spinel	25.3	0.9	2.2	19.5	0.9	A A
Comparative Example 9	20	spinel	50.3	11.8	1.1	46.8	1.0	B A

It is understood from the results shown in Table 6 that the iron content in the coating film is preferably 1.0% by weight or more for suppressing the electroconductivity of the coating film, but if the iron content is too large, the durability, particularly the acid resistance, of the coating film is deteriorated, and therefore the iron content is preferably 4.5% by weight or less. If the nickel content is too large, the crystalline structure of the metallic oxide in the coating film does not become spinel structure, resulting in problems such as high visible light transmission. Therefore, the nickel content is preferably from 5 to 40% by weight, also in view of the durability of the coating film.

Example 24

A 150 mm long, 150 mm wide, and 6 mm thick soda-lime silica glass plate was washed and dried to prepare a substrate. The substrate was fixed with a hanger in an electric oven set at 650°C and maintained for 5 minutes. A coating solution composed of 8.2 g of cobalt (III) acetylacetonate and 1.2 g of dipropionylmethanenickel (II) dissolved in 200 cc of toluene was sprayed onto the substrate taken out of the electric oven by using a commercially available spraygun at an air pressure of 1.5 kg/cm², an air flow of 50 l/min, and at a rate of spray coating of 120 ml/min for about 5 seconds.

The visible light transmission of the resulting heat ray-reflecting glass was measured in accordance with JIS R

3106-1985. The chromaticness indexes a^* and b^* according to the $L^*a^*b^*$ colorimetric system specified in JIS Z 8729-1980 were measured according to JIS R 3106-1985. The crystalline structure of the coating film was determined by X-ray diffraction spectroscopy. The surface resistivity of the coating film was measured by such a manner that the heat ray-reflecting glass was cut into 5x4 cm, silver paste was applied on the longer edge of 5 cm to a width of 0.5 cm to form an electrode, and the resistivity was measured with a digital multimeter. The wear resistance was measured by such a manner that a Taber truck wheel was rotated for 200 revolutions according to JIS R 3221-1990, and the difference in the haze values before and after the treatment was measured. The chemical resistance was measured by such a manner that the heat ray-reflecting glass was immersed in an acid solution or an alkaline solution specified in JIS R 3221 for 24 hours, and the deterioration of the coating film was evaluated to grade A, in which substantially no deterioration was observed, and grade B, in which obvious deterioration was observed. The results obtained are shown in Table 7 below.

Example 25

Heat ray-reflecting glass was prepared in the same manner as in Example 24, except that a coating solution composed of 8.2 g of cobalt (III) acetylacetonate, 1.2 g of dipropionylmethanenickel (II), and 0.7 g of iron (III) acetylacetonate dissolved in 200 cc of toluene was used. The

resulting heat ray-reflecting glass was examined in the same manner as in Example 24. The results obtained are shown in Table 7.

Example 26

Heat ray-reflecting glass was prepared in the same manner as in Example 24, except that soda-lime silica glass having a thickness of 12 mm was used as the glass substrate, and a coating solution composed of 8.2 g of cobalt (III) acetylacetonate, 1.2 g of dipropionylmethanenickel (II), and 0.7 g of iron (III) acetylacetonate dissolved in 200 cc of toluene was used. The resulting heat ray-reflecting glass was examined in the same manner as in Example 24. The results obtained are shown in Table 7.

Example 27

Heat ray-reflecting glass was prepared in the same manner as in Example 24, except that soda-lime silica glass having a thickness of 6 mm, the transmission color tone of which was blue, was used as the glass substrate. The resulting heat ray-reflecting glass was examined in the same manner as in Example 24. The results obtained are shown in Table 7.

Example 28

Heat ray-reflecting glass was prepared in the same manner as in Example 24, except that soda-lime silica glass having a thickness of 5 mm, the transmission color tone of which was green, was used as the glass substrate. The

resulting heat ray-reflecting glass was examined in the same manner as in Example 24. The results obtained are shown in Table 7.

Comparative Example 10

Heat ray-reflecting glass was prepared in the same manner as in Example 24, except that a coating solution composed of 3.6 g of cobalt (III) acetylacetonate and 1.8 g of chromium (III) acetylacetonate dissolved in 200 cc of toluene was used. The resulting heat ray-reflecting glass was examined in the same manner as in Example 24. The results obtained are shown in Table 7.

TABLE 7

	Thickness of coating film (nm)	Crystal structure	Visible light reflectance (%)	Color tone of reflected visible light		Surface resistivity (k Ω /square)	Wear resistance (%)	Chemical resistance	
				a*	b*			Acid	Alkali
Example 24	25	spinel	31.5	-5.1	-1.1	1.4	0.8	A	A
Example 25	30	spinel	32.1	-4.3	0.1	3.9	0.9	A	A
Example 26	27	spinel	31.1	-5.5	-0.9	2.2	0.8	A	A
Example 27	35	spinel	31.9	-8.3	-2.7	3.6	0.9	A	A
Example 28	33	spinel	32.8	-9.5	0.6	2.9	1.0	A	A
Comparative Example 10	30	spinel	33.2	-2.2	0.3	3 \times 10 ⁶	1.2	A	A

It is understood from the results shown in Table 7 that in Examples 24 to 26 using soda-lime glass as the substrate, the chromaticness indexes a^* and b^* according to the $L^*a^*b^*$ colorimetric system are in the following ranges:

$$-7.0 \leq a^* \leq -3.0$$

$$-5.0 \leq b^* \leq 4.0$$

The reflected light having a color tone within the above ranges is of green tone that are generally favorable in appearance.

The heat ray-reflecting glass according to the present invention is such that can be produced by a method based on thermal decomposition of a coating solution, which method is excellent in productivity. The present invention affords an improvement on electromagnetic wave reflection, durability of coating film, and color tone of reflected light, which might be a serious problem in practical use for the considerations on environmental conservation, while retaining the characteristics of heat ray-reflecting glass having a coating film containing cobalt oxide and nickel oxide, i.e., the visible light transmission and solar radiation transmission can be controlled below a certain level.

CLAIMS

1. Heat ray-reflecting glass comprising a glass substrate having on the surface thereof a coating film comprising cobalt oxide and nickel oxide,

said coating film having a surface resistivity of not less than $10^4 \Omega/\text{square}$ and a thickness of not less than 10 nm,

the content of cobalt in said coating film based on the total metal content per unit area being from 60 to 90% by weight,

the content of nickel in said coating film based on the total metal content per unit area being from 10 to 40% by weight.

2. Heat ray-reflecting glass as claimed in claim 1, wherein the content of cobalt in said coating film based on the total metal content per unit area is from 68 to 87% by weight, and the content of nickel in said coating film based on the total metal content per unit area is from 13 to 32% by weight.

3. Heat ray-reflecting glass comprising a glass substrate having on the surface thereof a coating film comprising cobalt oxide and nickel oxide,

said coating film further comprising a metal oxide containing at least one metal selected from titanium, vanadium, chromium, manganese, copper, and zirconium, and

having a surface resistivity of not less than 10^4 Ω /square and a thickness of not less than 10 nm,

the content of cobalt in said coating film based on the total metal content per unit area being from 60 to 89% by weight,

the content of nickel in said coating film based on the total metal content per unit area being from 10 to 39% by weight,

the content of at least one metal selected from titanium, vanadium, chromium, manganese, copper, and zirconium in said coating film based on the total metal content per unit area being from 1 to 30% by weight.

4. Heat ray-reflecting glass as claimed in one of claims 1 to 3, wherein said coating film has a thickness of not more than 130 nm.

5. Heat ray-reflecting glass comprising a glass substrate having on the surface thereof a coating film comprising cobalt oxide and nickel oxide,

said coating film further comprising an iron oxide, and having a surface resistivity of not less than 10^4 Ω /square and a thickness of from 10 to 70 nm,

the content of iron in said coating film based on the total metal content per unit area being from 1.0 to 4.5% by weight.

6. Heat ray-reflecting glass as claimed in claim 5, wherein the content of nickel in said coating film based on

the total metal content per unit area is from 5 to 40% by weight.

7. Heat ray-reflecting glass as claimed in one of claims 1 to 6, wherein a reflecting color tone viewed from the side of said heat ray-reflecting glass opposite to said coating film is green series color.

8. Heat ray-reflecting glass as claimed in one of claims 1 to 7, wherein said coating film consisting essentially of oxides having spinel structures.

9. Heat ray-reflecting glass as claimed in one of claims 1 to 8, wherein a transmitted visible light exhibits a transmitted color tone falling within the following ranges:

$$-4.5 \leq a^* \leq 4.5$$

$$3.0 \leq b^* \leq 12.5$$

wherein a^* and b^* represent chromaticness indexes.

10. Heat ray-reflecting glass as claimed in one of claims 1 to 9, wherein a reflected visible light viewed from the side of said heat ray-reflecting glass opposite to said coating film exhibits a reflected color tone falling within the following ranges:

$$-7.0 \leq a^* \leq -3.0$$

$$-5.0 \leq b^* \leq 4.0$$

wherein a^* and b^* represent chromaticness indexes.

11. Heat ray-reflecting glass comprising a glass substrate having on the surface thereof a coating film comprising cobalt oxide and nickel oxide,

said coating film consisting essentially of oxides having spinel structures comprising cobalt oxide and nickel oxide, and having a surface resistivity of not less than $10^4 \Omega/\text{square}$ and a thickness of from 10 to 70 nm,

a reflecting color tone viewed from the side of said heat ray-reflecting glass opposite to said coating film being green series color.

Patents Act 1977 Examiner's report to the Comptroller under Section 17 (The Search report)	Application number GB 9426370.4
Relevant Technical Fields (i) UK CI (Ed.N) C7F (FHB, FHD, FHE) (ii) Int CI (Ed.6) C03C (17/23, 17/245, 17/25); C23C (16/40, 18/12)	Search Examiner P G BEDDOE
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Category	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2016434 A (PPG) see Examples, Table 1	1, 11
X	GB 1397741 (GLAVERBEL) see especially page 3 lines 88-95	1, 11
X	US 4160061 (CENTRAL GLASS) see especially Table 5	1, 11
X	US 3850665 (GLAVERBEL) see especially column 8 lines 25-29	1, 11
X	US 3185586 (PITTSBURGH) see especially Tables III, IV	1, 11
X	US 2975076 (PITTSBURGH) see especially Example IV	1, 11
X	US 2688565 (PITTSBURGH) see especially column 4, lines 29-42	1, 11
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